Supplementary Information: Non-equilibrium thermodynamics of the Markovian Mpemba effect and its inverse

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I. ENTROPIC DISTANCE FUNCTION $D_e[\vec{p}(t);T_b]$

Here we show that $D_e[\vec{p}(t);T_b]$, defined by Eq. 5 in the main text, is the total entropy production of the system plus the environment along the relaxation process from $\vec{p}(t)$ at time t to the final equilibrium $\vec{\pi}(T_b)$ at $t=\infty$. For simplicity, we choose a unit system where $k_B=1$.

In stochastic thermodynamics, the total entropy production rate of a system $\vec{p}$ and the heat bath is given by [1, 2]

$$\dot{S}(t) \;=\; \sum_{i<j}(R_{ij}p_j - R_{ji}p_i)\ln\frac{R_{ij}p_j}{R_{ji}p_i}. \tag{S1}$$

According to this definition, $\dot{S}$ is non-negative because the signs of $R_{ij}p_j - R_{ji}p_i$ and $\ln(R_{ij}p_j)/(R_{ji}p_i)$ are always identical. When the system is in the thermal equilibrium $\vec{p}(t)=\vec{\pi}(T_b)$, there is no entropy production and $\dot{S}$ equals zero (the system is detailed balanced). The distance function $D_e[\vec{p}(t);T_b]$ can be obtained by integrating $\dot{S}$ from time t to ∞:

$$D_e[\vec{p}(t);T_b] = \int_t^\infty \dot{S}\,(t')\,dt'. \tag{S2}$$

Let us denote the net probability current from state j to state i by

$$J_{ij} = R_{ij}p_j - R_{ji}p_i = -J_{ji} \tag{S3}$$

and formulate $\dot{p}_i$ by

$$\dot{p}_i = \sum_j J_{ij} \quad . \tag{S4}$$

Substituting Eq.S1 into Eq.S2 gives

$$\begin{aligned}
D_e[\vec{p}(t);T_b] \;&=\; \int_t^\infty \sum_{i<j} J_{ij}\ln\frac{R_{ij}p_j}{R_{ji}p_i}dt' = \int_t^\infty \sum_{i<j} J_{ij}\left(\ln p_j - \ln p_i + \frac{E_j-E_i}{T_b}\right)dt' \\
&=\; \int_t^\infty \sum_i -\dot{p}_i\ln p_i - \frac{\dot{p}_i E_i}{T_b}dt' \\
&=\; -\sum_i \frac{(\pi_i-p_i)E_i}{T_b} + \int_t^\infty \dot{p}_i\ln p_i dt' \\
&=\; -\sum_i \frac{(\pi_i-p_i)E_i}{T_b} + \int_t^\infty \frac{d}{dt}(p_i\ln p_i) - \dot{p}_i dt' \\
&=\; -\sum_i \frac{(\pi_i-p_i)E_i}{T_b} + \pi_i\log\pi_i - p_i\ln p_i - \pi_i + p_i \\
&=\; \sum_i \frac{(p_i-\pi_i)E_i}{T_b} + p_i\ln p_i - \pi_i\log\pi_i
\end{aligned} \tag{S5}$$

where we used integration by parts and $\sum_i p_i = \sum_i \pi_i = 1$.

In stochastic thermodynamics, the above result has a simple interpretation [2]. The first term, $\sum_i \frac{(p_i-\pi_i)E_i}{T_b}$, is the entropy production in the bath. The second and third terms, $\sum_i(p_i\ln p_i - \pi_i\log\pi_i)$ are the changes in the Shannon entropy of the system. Generalization of the above to continuous systems is straightforward.

II. THE DISTANCE FROM EQUILIBRIUM GROWS WITH THE INITIAL TEMPERATURE

Here we show that $D_e[\vec{\pi}(T_c);T_b] < D_e[\vec{\pi}(T_h);T_b]$ for any $T_h > T_c > T_b$. In other words, the distance function we chose has the property that the hot system starts at a greater initial distance from equilibrium at T_b compared with the colder system. Notice that initially, both the hot and the cold systems start from a Boltzmann distribution at initial temperature $T_{ini} = T_h$ and T_c, and the initial distance function takes the form

$$D_e[\vec{\pi}(T_{ini});T_b] = \sum_i \frac{E_i(\pi_i(T_{ini}) - \pi_i(T_b))}{T_b} + \pi_i(T_{ini})\log\pi_i(T_{ini}) - \pi_i(T_b)\log\pi_i(T_b) \tag{S6}$$

and thus

$$\begin{aligned} D_e[\vec{\pi}(T_h);T_b] - D_e[\vec{\pi}(T_c);T_b] &= \sum_i \frac{E_i(\pi_i(T_h) - \pi_i(T_c))}{T_b} + \pi_i(T_h)\log\pi_i(T_h) - \pi_i(T_c)\log\pi_i(T_c) && \text{(S7)} \\ &\geq \sum_i \frac{E_i(\pi_i(T_h) - \pi_i(T_c))}{T_c} + \pi_i(T_h)\log\pi_i(T_h) - \pi_i(T_c)\log\pi_i(T_c) && \text{(S8)} \\ &\geq 0 && \text{(S9)} \end{aligned}$$

where the second inequality is due to the non-negativity of $D_e[\vec{p};T_c]$ for any $\vec{p}$ and T_c (as is shown in section I of SI). The first inequality is due to the fact that $T_c > T_b$ and that

$$\sum_i E_i(\pi_i(T_h) - \pi_i(T_c)) = \langle E\rangle_{T_h} - \langle E\rangle_{T_c} \geq 0 \tag{S10}$$

Note that the above inequality is valid for $T_h > T_c > T_b$ when the system's heat capacity is non-negative. We can show that for our system of interest, the heat capacity defined as follows is non-negative:

$$\begin{aligned} \frac{\mathrm{d}\langle E\rangle_T}{\mathrm{d}T} &= \frac{\mathrm{d}}{\mathrm{d}T}\frac{\sum_i E_i e^{-E_i/T}}{Z(T)} && \text{(S11)} \\ &= \frac{\langle E^2\rangle_T - \langle E\rangle_T^2}{T^2} && \text{(S12)} \end{aligned}$$

where

$$Z(T) = \sum_i e^{\frac{-E_i}{T}} \tag{S13}$$

is the partition function.

This proof guarantees that the distance function of the initially hotter system always starts at a higher value compared to that of the initially colder system.

III. THE CHOICE OF $D[\vec{p},T_b]$ IS NOT UNIQUE.

In the main text we gave an argument showing that the Mpemba effect should occur when λ_2 is strictly larger than λ_3 and $|a_2^h| < |a_2^c|$. Here we give a more careful derivation of the same argument, using the three properties we demand from the distance-from-equilibrium function. This allows us to characterize the Mpemba effect with any good choice of distance function $D[\vec{p},T_b]$. First, we note that

$$\vec{p}(t) = \vec{\pi}(T_b) + e^{\lambda_2 t}a_2\vec{v}_2 + ... + e^{\lambda_n t}a_n\vec{v}_n. \tag{S14}$$

For large enough t, the terms $e^{\lambda_3 t}a_3\vec{v}_3 + ... + e^{\lambda_n t}a_n\vec{v}_n$ are exponentially smaller than $e^{\lambda_2 t}a_2\vec{v}_2$. Hence, we can expand $D[\vec{p}(t),T_b]$ around $e^{\lambda_2 t}a_2\vec{v}_2$:

$$D[\vec{p}(t),T_b] \approx D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2\vec{v}_2,T_b] + \sum_i a_i e^{\lambda_i t}\vec{v}_i\cdot\nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2\vec{v}_2,T_b] \tag{S15}$$

Let us next look on the difference $D[\vec{p}^h(t),T_b] - D[\vec{p}^c(t),T_b]$. Using the above expansion, we can approximate the difference as:

$$\begin{aligned} D[\vec{p}^h(t),T_b] - D[\vec{p}^c(t),T_b] &\approx D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^h\vec{v}_2,T_b] - D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2,T_b] \\ &\quad + \sum_i e^{\lambda_i t}\left(a_i^h\vec{v}_i\cdot\nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^h\vec{v}_2,T_b] - a_i^c\vec{v}_i\cdot\nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2,T_b]\right) && \text{(S16)} \end{aligned}$$

But at large enough t, the term $(a_2^h - a_2^c)e^{\lambda_2 t}$ is also very small, therefore we can further expand

$$D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^h\vec{v}_2, T_b] - D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2, T_b] \approx \vec{v}_2 \cdot \nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2, T_b](a_2^h - a_2^c)e^{\lambda_2 t}. \tag{S17}$$

Substituting Eq.(S17) in Eq.(S16) gives:

$$\begin{aligned} D[\vec{p}^h(t), T_b] - D[\vec{p}^c(t), T_b] \;\approx\; & \vec{v}_2 \cdot \nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2, T_b](a_2^h - a_2^c)e^{\lambda_2 t} \\ & + \sum_i e^{\lambda_i t}\left(a_i^h\vec{v}_i \cdot \nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^h\vec{v}_2, T_b] - a_i^c\vec{v}_i \cdot \nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2, T_b]\right) \end{aligned} \tag{S18}$$

The first term, $\vec{v}_2 \cdot \nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2, T_b](a_2^h - a_2^c)e^{\lambda_2 t}$ is positive since $a_2^h > a_2^c$ and since the distance grows in the $\vec{v}_2$ direction. This can be seen by applying on the initial condition $\vec{p} = \vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2$ the demand that the distance-from-equilibrium is monotonically decreasing with time. The second term (the sum in the right hand side of the above equation) might be negative, but it is proportional to $e^{\lambda_i t}$ and hence it is negligible compared to the first term which is proportional to $e^{\lambda_2 t}$. One might worry that in the $t \to \infty$ the pre-factor of $e^{\lambda_2 t}$, given by $\vec{v}_2 \cdot \nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2, T_b]$, decays exponentially faster than the pre-factor of $e^{\lambda_i t}$ (given by $\left(a_i^h\vec{v}_i \cdot \nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^h\vec{v}_2, T_b] - a_i^c\vec{v}_i \cdot \nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^c\vec{v}_2, T_b]\right)$), and hence the $e^{\lambda_i t}$ factors cannot be neglected. However, this cannot be the case since we demand the distance function is convex, hence $\nabla D[\vec{\pi}(T_b) + e^{\lambda_2 t}a_2^h\vec{v}_2, T_b]$ approaches zero at most linearly with $e^{\lambda_2 t}$.

IV. THE MARKOVIAN MPEMBA EFFECT IN 1-DIMENSIONAL CONFIGURATION SPACE

In the main text we gave a numerical example for the Mpemba effect in continuous configuration space, solved by the Fokker-Planck diffusion operator (see also Fig. 5B in the main text). Here we discuss this example in detail. To this end we consider the diffusion of a Brownian particle in a potential $V(x)$ (heat bath's temperature is T_b). The probability to find the Brownian particle in position x at time t is given by $p(x,t)$, which evolves according to

$$\partial_t p(x,t) = \partial_x\Big(\mu(\partial_x V) + D\partial_x\Big)p(x,t) = \mathcal{L}p \tag{S19}$$

where we assume that the diffusion and mobility coefficients, D and μ, are homogenous in both time and space. These two coefficients are related by the Einstein-Smoluchowski relations, $D = \mu k_B T$. In the following, we assume $\mu = 1$ and $k_B = 1$, hence the Fokker-Planck equation operator is simplified into

$$\mathcal{L} = \partial_x\Big((\partial_x V) + T_b\partial_x\Big). \tag{S20}$$

The unique steady state (equilibrium distribution) of $\mathcal{L}$ is given by the Boltzmann distribution,

$$\pi(x) = \frac{e^{-V(x)/T_b}}{Z} \tag{S21}$$

where

$$Z = \int e^{-V(x)/T_b}dx \tag{S22}$$

is the partition function of the system at bath's temperature. The entropic distance function is given by

$$D[\vec{p}(t); T_b] = \int\left(\frac{V(x)(p(x) - \pi(x))}{T_b}\right) + p(x)\ln p(x) - \pi^b(x)\ln\pi^b(x)dx. \tag{S23}$$

In the specific example we used the potential

$$\begin{aligned} V(x) \;=\; & 3\left(\arctan(x-11) - \arctan(x-9)\right) \\ & +3.1\left(\arctan(x-31) - \arctan(x-29)\right) \\ & +0.2\left(\arctan(x-70) - \arctan(x-20) + 0.05x\right) \end{aligned} \tag{S24}$$

The term in the first line generate a well around $x = 10$, the second one a slightly deeper well at $x = 30$, and the third line extend the basin of the deeper well. This potential is plotted in the upper left panel of Fig. S1.

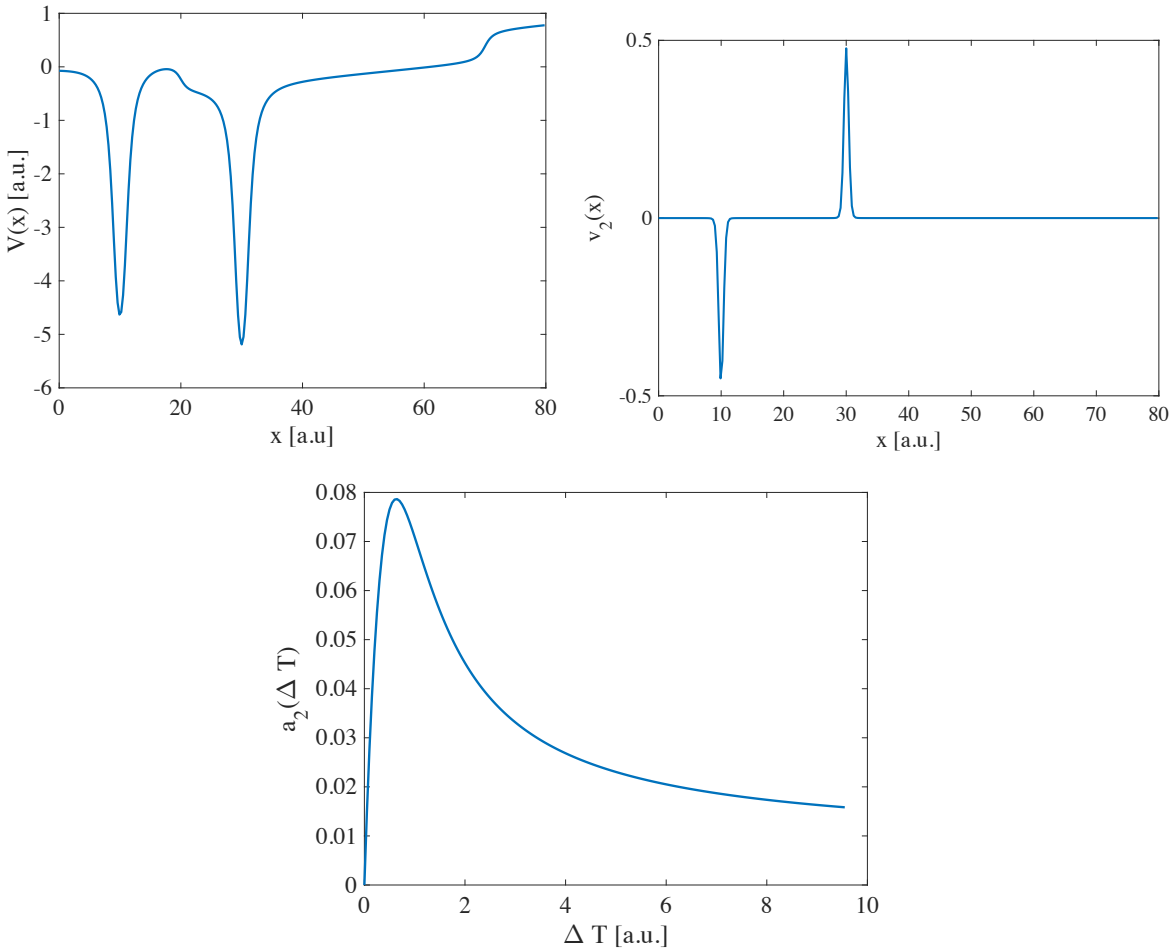

FIG. S1: **Mpemba effect in Diffusion Process:** The upper-left panel shows the potential energy landscape. The smallest nonzero eigenvalue eigenfunction is plotted on the left. As can be seen, it corresponds to a flow from one well to the other. Lower pannel - the coefficient of the smallest non-zero eigenvalue eigenfunction in the Boltzmann distribution as a function of the temperature difference from T_b. The coefficient decreases at high temperature, hence the Mpemba effect appears.

When two systems initially prepared at the equilibriums of $T_c = 1.38$ and $T_h = 10$, are simultaneously cooled by a bath at $T_b = 0.45$, they demonstrates the Mpemba effect (see Fig. 5C of main text). The cooling relaxation is numerically simulated by discretizing the x-axis into 1000 points and integrating over time. The slowest relaxation mode, $v_2(x)$, is shown in the upper right panel of Fig. S1. As expected, it corresponds to a slow transition from one well into the other one. $a_2(\Delta T)$, which is the contra-variant coefficients of $\vec{v}_2(x)$ in a points along the quasi-static locus with temperature $T_b + \Delta T$, is plotted in the lower panel of Fig. S1. As can be seen, it decreases beyond some ΔT, hence the Mpemba effect appears.

V. IS IT DIFFICULT TO CONSTRUCT A 3-STATES SYSTEM WITH THE MARKOVIAN MPEMBA EFFECT?

In the main text, we provided a sufficient condition for the Mpemba effect (i.e. $a_2^h < a_2^c$) and an example with a 3-state model. One may be curious how common can an arbitrary 3-state system allows for the Mpemba effect. Here we show that it it not difficult to construct such a 3-state system. In our view, the Mpemba effect is a property of the system itself: we consider a system, characterized by a set of energies E_i and barriers B_{ij}, and ask if there exist three temperatures $T_b < T_c < T_h$, such that the Mpemba effect occurs. In the following we would like to understand in what fraction of the 3-state model parameter-space (E_i and B_{ij}), the Mpemba effect can occur for some $T_b < T_c < T_h$. As we demonstrate below, the Mpemba effect is not restricted to a carefully chosen set of parameters, on the contrary: there exist a wide range of values in the parameter space that allows for the Mpemba effect.

For the sake of argument, we consider the limit of $T_b \to 0$. Without lose of generality, we further reduce the parameter space by setting $E_1 = 0$, $E_3 = 1$ and $E_2 = E$ where $0 < E < 1$. With these choices (which amounts to choosing units of time and energy), the ultimate equilibrium state is given by $\vec{v}_1 = \vec{\pi}(0) = (1, 0, 0)$, since at zero temperature the system is to be found only at the lowest energy state. Furthermore, in the limit of $T_b \to 0$, all the element of R_{ij} are negligible except for the dominant off-diagonal element, i.e. the one with the smallest activation energy $B_{ij} - E_j$. Therefore, depending on the position of the dominant off-diagnal element, the transition rate matrix R is proportional to one of the following matrices:

$$A = \begin{pmatrix} 0 & 1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}; \; B = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \; C = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & -1 \end{pmatrix} \tag{S25}$$

Each of these matrices has a fast relaxation direction corresponding to the $\lambda_3 = -1$ eigenvalue: (i)When $B_{12} < B_{13}$ and $B_{12} - E < B_{23} - 1$, all the elements in R are negligible except for R_{12} and R_{22}, and thus R is proportional to the matrix A above, and $\vec{v}^3 = (1, -1, 0)$. In this case $a_2^h > a_2^c$ for all T_h and T_c, and there is no Mpemba effect. (ii) When $B_{23} < B_{13}$ and $B_{23} - 1 < B_{12} - E$, the matrix R is proportional to the matrix B above, and $\vec{v}^3 = (0, 1, -1)$. In this case $a_2^h > a_2^c$, and there is no Mpemba effect. (iii) When $B_{13} - 1 < B_{12} - E$ and $B_{13} < B_{23}$, the matrix R is proportional to the matrix C above, and $\vec{v}^3 = (1, 0, -1)$. In this case there is a Mpemba effect if the curve $\vec{\pi}(T)$ is tangent to $\vec{v}^3$, which is the case when $E < \frac{1}{2}$. Therefore, in any system where

$$E < \frac{1}{2}; \tag{S26}$$

$$B_{13} - 1 < B_{12} - E; \tag{S27}$$

$$B_{13} < B_{23} \tag{S28}$$

the Mpemba effect occurs for sufficiently low T_b.

This shows that the Mpemba effect can be found in a wide range of parameters E and B_{ij}. Consider randomly picking values of E, and B_{ij}'s according to a uniform distribution within the range $(0, 1)$, the chance that the above three equations holds (i.e. there exist $T_h > T_c$ where the Mpemba effect occurs) is at least $1/8$: If E is sampled from the interval $(0, 1)$ with uniform distribution then the probability for the first condition $E < \frac{1}{2}$ is 0.5. Similarly if the B_{ij}'s are sampled from some interval with identical uniform distribution, then the probability for $B_{13} < B_{23}$ is 0.5, and the probability for $B_{13} - 1 < B_{12} - E$ is larger than 0.5. If all these parameters are independent, then the probability that the system is compatible with the Mpemba effect is therefore at least $\frac{1}{8}$. This calculation is clearly only a lower bound, since we only considered a single temperature, $T_b = 0$. In principle it is possible that at other values of T_b there are cases with the Mpemba effect outside the range discussed above, hence the probability can be larger.

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